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E.D. Edney, D.C. Stiles, J.W. Spence, F.H. Haynie and W.E. Wilson

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16. ABSTRACT

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The laboratory results suggest that the damage to galvanized steel induced by the dry deposition of SO_2 can be calculated by equating the dry SO_2 flux to the Zn corrosion flux. SO_2 will deposit onto a dry surface until an amount similar to that of a monolayer has formed. Under wet conditions, the dry deposition flux is controlled by the gas-phase resistance of the atmosphere. Wet deposition of acidic species induces corrosion which depends not only on the pH of the incident rain, but also on the exposure history of the samples.

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LABORATORY INVESTIGATIONS OF THE IMPACT OF DRY DEPOSITION OF SO_2 AND WET DEPOSITION OF ACIDIC SPECIES ON THE ATMOSPHERIC CORROSION OF GALVANIZED STEEL

EDWARD O. EDNEY and DAVID C. STILES
Northrop Services, Inc.-Environmental Services, P.O. Box 12313, Research Triangle Park, NC 27709, U.S.A.

and

JOHN W. SPENCE, FRED H. HAYNIE and WILLIAM E. WILSON
Atmospheric Sciences Research Laboratory, United States Environmental Protection Agency, Research Triangle Park, NC 27711, U.S.A.

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Abstract—A series of short-term laboratory experiments were conducted in which galvanized steel samples were exposed to sub-ppm levels of SO_2. Dew was produced periodically on the test panels, and, at the end of some experiments, panels were sprayed with solutions of various pH levels. Both dew and rain rinse samples were analyzed for $SO_3^{=}$, $SO_4^{=}$ and Zn.

The laboratory results suggest that as a first approximation the damage to galvanized steel induced by the dry deposition of SO_2 can be calculated by equating the dry SO_2 flux to the Zn corrosion flux. SO_2 will deposit onto a fresh dry surface until an amount similar to that of a monolayer has formed. Under wet conditions, the dry deposition flux is controlled by the gas-phase resistance of the atmosphere. Wet deposition of ammonium bisulphate induces corrosion which depends not only on the pH of the incident rain, but also on the exposure history of the samples.

1. INTRODUCTION

Galvanizing steel is a well-known technique for protecting steel against corrosion. Galvanized steel consists of a Zn coating strongly bonded to a steel substrate. Zn is anodic with respect to Fe and therefore will react electrochemically before Fe in the presence of an electrolytic solution. Because it is one of the best and least expensive methods for protecting steel against atmospheric corrosion, many investigations have been conducted to assess the rate of corrosion in various atmospheric environments. However, during most of the field studies, measurements of important chemical and physical parameters have not been made; in particular, those associated with wet deposition. This information is necessary for the development of models that can predict the corrosion rate for a given set of environmental conditions.

Recently, a number of field studies have been conducted in which key parameters such as SO_2 concentration and time of wetness, which are known to affect the corrosion rate, have been measured (Haynie, 1980; Mansfield, 1980; Mikailvosky, 1982; Atteraas and Haagenrud, 1982). However, only Atteraas and Haagenrud (1982) considered the impact of wet deposition. The developed models have been presented in the form of damage functions, which establish the functional relationship between the key physical and chemical parameters and the Zn corrosion rate. The first step in constructing the damage function is the selection of an adequate set of variables. Once this set has been chosen, a selection is made for the form of the damage function. The constants contained in the damage function are obtained by a regression analysis of the field data. If damage functions are shown to predict accurately the corrosion rates for a variety of environmental conditions, they can be employed to estimate economic losses due to corrosion. The development of damage functions for galvanized steel that incorporate the effects of wet deposition has not yet reached this stage. To develop damage functions that are more universal, field studies measuring the amount and chemical composition of rain should be conducted. Meteorological parameters, such as deposition velocities which affect the delivery rates of chemical species, should be determined. It is also not clear what role chemicals other than SO_2 may play in atmospheric corrosion. In principle, it may be necessary to include the effects of all of these parameters to obtain a reliable damage function.

One approach to define the key physical and chemical parameters better is to conduct controlled laboratory studies that attempt to determine the impact of the above mentioned parameters. The results reported here are those obtained during short-term laboratory experiments in which panels of galvanized steel were exposed to a series of concentrations of SO_2 under carefully controlled aerodynamic conditions.

The panels were chilled to produce dew and, at the end of some of the experiments, were sprayed to simulate wet deposition. Both dew and rain rinse samples were analyzed to determine their chemical composition. The results of these experiments and their implications for interpreting field study data are presented.

2. EXPERIMENTAL

Figure 1 illustrates the exposure system which consists of two exposure chambers in parallel coupled to an 11.3-m^3 Al smog chamber. The smog chamber, operated as a continuous stirred tank reactor, serves as a reservoir for the exposure chambers. Ambient air first passes through a clean air train, where pollutants and H_2O are removed, and then through a glass manifold, where it is mixed with SO_2 to the desired concentration before entering the smog chamber. The flow rate through the smog chamber is 95 $l\ min^{-1}$, producing a value of ~ 2 h for the residence time. Steam is injected into the chamber by the dew point control system that is programmed to maintain the dew point at 15°C. The air temperature in the system is not controlled.

A cross-sectional drawing of one of the exposure chambers is shown in Fig. 2. The chambers are constructed of clean Teflon glued to a 13-cm × 13-cm × 152-cm welded Al frame. Glass piping is used to connect the exposure chambers to the smog chamber. Both exposure chambers have seven positions for mounting test panels. Each exposure position has a chiller back plate with supplied coolant so that the panel can be chilled below the air dew point to produce dew on the panels. Individual positions can be disconnected from the coolant manifold to remain dry. The coolant temperature enables dew to form in a sufficient quantity to drop into the collection trough below each panel. The collected dew then drains into a Nalgene bottle. The exposure chambers are also equipped with heating lamps.

Blowers were mounted on the exposure chambers to maintain turbulent conditions (Reynolds number ~ 30,000) in the chambers. The blower settings were selected to produce wind speeds of approximately 3 $m\ s^{-1}$ in each chamber.

At the completion of some of the exposure experiments, galvanized steel panels were sprayed with either deionized water (pH = 5.6) or ammonium bisulphate (NH_4HSO_4) solutions. The pH of the spray solutions was controlled by diluting a 2-mmol solution of NH_4HSO_4 in deionized H_2O. Solutions with pHs of 5.0, 4.7, 4.0, 3.7 and 3.0 were prepared. By removing the panels from the exposure chambers and mounting them into a Teflon rack, each panel could be sprayed with a specific volume of either deionized H_2O or a diluted NH_4HSO_4 solution. The spray runoff was collected for chemical analysis. For a typical spray condition, ~ 10 s was the average residence time of a droplet on the surface, whereas the corresponding time for a dew droplet was ~ 1 h.

Fig. 1. Schematic of exposure system.

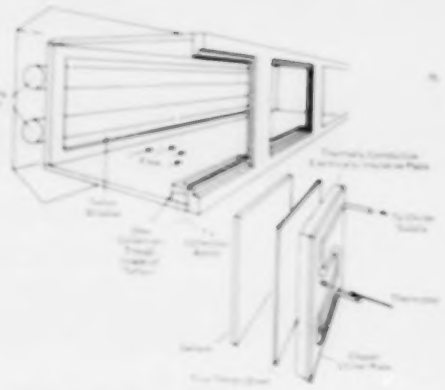

Fig. 2. Cross sectional view of exposure chamber.

Chamber SO_2 concentrations were determined using a Thermo Electron Corporation SO_2 monitor. The detector is a pulsed-fluorescent photometer that operates over a range of wavelengths from 230 to 190 nm. The instrument was zeroed using clean tank air that had passed through brominated charcoal, reducing the SO_2 concentration to less than 0.5 ppb. A permeation tube, used to generate SO_2, was mounted in an oven in which the temperature was maintained to ±0.1°C. The permeation tube was weighed on a microgram balance over a period of several days to calculate the permeation rate.

A CTE dew point hygrometer was used in the dew point control system. It uses a LiCl cell for the detector, and is calibrated by placing the sensor in a closed container with a saturated solution of NaBr (relative humidity = 58%, at 20°C).

The collected dew and rain rinse samples were analyzed for Zn using an Instrument Labs Inc. atomic absorbance analyzer. The instrument ionizes the liquid samples in an air/acetylene flame and measures the absorbance at a wavelength of 213.9 nm. The system was calibrated by measuring the absorbance of a series of American Chemical Society (ACS) certified Zn standards.

The samples were also analyzed for SO_4^{2-} and SO_3^{2-} by ion chromatography. The analysis was performed on a Dionex Auto Ion System 12 analyzer equipped with 6-mm × 40-mm cation suppressing pre-column, a 6-mm × 250-mm fast run anion separator column, and a fiber suppressor. The eluent used was a 3-mmol sodium bicarbonate ($NaHCO_3$), 2.4-mmol sodium carbonate (Na_2CO_3) aqueous solution with a flow rate of 3 ml min^{-1}. The fiber suppressor used an aqueous solution of H_2SO_4 (0.025N) with a flow of 11 ml min^{-1}. Calibration curves were generated using anhydrous sodium sulfate (Na_2SO_4) and sodium sulfite (Na_2SO_3) salts diluted with deionized H_2O. The sulfite standards required an addition of 0.7% formaldehyde (HCHO) to the stock solution to deter oxidation of sulfite to sulfate.

Short-term SO_2 exposure experiments were conducted at average SO_2 concentrations of 3, 7, 30, 45, 95, 240 and 650 ppb. SO_2 concentrations were maintained, with the exception of the 3-ppb and 7-ppb experiments, by introducing SO_2 from a high concentration tank into the inlet manifold at a rate sufficient to give the desired concentration. For the two low concentration experiments, no SO_2 was introduced into the manifold; instead, the source of SO_2 came from the walls of the various surfaces in the exposure/smog chamber system.

Table 1. Summary of experimental conditions

$[SO_2]$ (ppb)	Air temperature (°C)	Time of wetness (t_w) (h)	Plate temperature when wet (°C)	Dew point (°C)	Relative humidity (%)	Conditioning time (t_c) (h)
3	19.8	20.5	12.6	15.0	74	21.6
7	32.1	6.3	10.3	15.0	36	4.8
30	23.9	7.0	12.6	15.0	57	0.1
45	23.5	7.0	12.7	15.0	59	16.0
95	25.4	7.0	12.6	15.0	53	2.5
95	23.3	20.0	12.6	15.0	60	—
240	23.3	17.0	12.7	15.0	60	1.1
650	29.7	7.0	10.0	15.0	41	6.0

[Due to a malfunction of the SO_2 monitor, no gas phase SO_2 measurements were made during the 7-ppb SO_2 experiment. The SO_2 concentration was determined from the SO_4^{2-} flux (see Table 1).]

The galvanized steel panels were 8 cm × 13 cm Zn-coated (hot-dipped), 20-gauge steel plates. The average thickness of the coating was 20 μm, and the exposed surface area per panel was 84.7 cm^2.

In a typical experiment, the panels were first cleaned by immersion into a 10% by weight solution of ammonium chloride (NH_4Cl) at a temperature of 60–80°C for 2 min. The panels were first rinsed in deionized H_2O and then dried in methanol (CH_3OH) to remove the moisture. Before mounting the cleaned panels into the exposure chamber, each exposure position of the dew collection system was rinsed with 50 ml of deionized H_2O. The microprocessor-controlled system was programmed for the chiller system to come on at a specified time and the panels to chill to a specific temperature below the air dew point for a fixed period of time. Fourteen panels of galvanized steel were then mounted into the exposure chambers—12 were connected to the chiller system and two were left dry for the entire experiment. Typically, the panels were exposed for a number of hours under dry conditions before the chill cycle began. At the end of the chill period, the samples were left in the chamber long enough to become visibly dry and then they were removed. During one of the experiments (95-ppb), the samples were exposed to two dew periods. At the end of the 3-ppb, 30-ppb and 45-ppb SO_2 experiments, the samples were sprayed with solutions containing varying pH levels. At the end of the experiment, the volume of collected dew was determined. The dew was then analyzed for SO_3^{2-} and SO_4^{2-} by ion chromatography and for Zn by atomic absorption spectroscopy. The rain rinse was analyzed in a similar way.

3. RESULTS

A summary of the experimental exposure conditions is given in Table 1. The table gives the SO_2 concentration ($[SO_2]$), air temperature, time of wetness (t_w), conditioning time (t_c), dew point, relative humidity, and panel temperature when the panels were wet for each exposure experiment. The $[SO_2]$ is the average gas-phase concentration. The conditioning time is the length of time between the loading of panels into the exposure chambers and the beginning of the dew cycle. The dew point was 15°C for each experiment. Due to lack of temperature control, both the air temperature and the relative humidity varied from one experiment to the next. Time of wetness is determined from the time the panel temperature begins to drop below the dew point to the time the plates are visibly dry. For example, it takes 1 h for the panels to dry after 6 h of chilling.

Dry deposition

The SO_3^{2-}, SO_4^{2-} and Zn concentrations measured in the collected dew are shown in Table 2. The volume of dew collected for each experiment and the calculated dew flux for SO_3^{2-}, SO_4^{2-}, SO_x^{2-}, and Zn are given in Table 3. The SO_x^{2-} flux is equal to the sum of the SO_3^{2-} flux and the SO_4^{2-} flux. The molar SO_3^{2-}, SO_4^{2-}, SO_x^{2-} and Zn flux are defined as shown in Equation (1):

$$F_X = \frac{[X]V}{At_w}, \tag{1}$$

Table 2. Chemical composition of dew

$[SO_2]$ (ppb)	Concentration (nmol ml^{-1})		
	SO_3^{2-}	SO_4^{2-}	Zn
3	0	38	139
7	0	65	157
30	101	319	351
45	159	483	609
95	189	797	842
95	210	1080	964
240	390	3260	3650
650	810	2283	3300

Table 3. Dew fluxes calculated using Equation (1)

$[SO_2]$ (ppb)	Volume of dew/plate (ml)	Dew flux (nmol cm^{-2} h^{-1})			
		SO_3^{2-}	SO_4^{2-}	SO_x^{2-}	Zn
3	16.2	0	0.4	0.4	1.3
7	16.5	0	2.0	2.0	4.9
30	5.3	0.9	2.9	3.8	3.1
45	4.4	1.2	3.6	4.8	4.5
95	4.7	1.5	6.3	7.8	6.7
95	17.9	2.2	11.4	13.6	10.2
240	12.6	3.4	28.5	31.9	31.9
650	16.6	22.7	63.9	86.6	92.4

where F_X is the dew flux of species X in nmol cm^{-2} h^{-1}, $[X]$ is the concentration of X in nmol ml^{-1}, A is the area per panel (84.7 cm^2), V is the volume of dew collected (ml), and t_w is the time of wetness (h).

The Zn flux defined above takes into account only the Zn corrosion products that are soluble in the dew. Zinc flux obtained by analysis of the dew can be equated with Zn corrosion rates determined by gravimetric techniques, where all corrosion products are chemically removed, if there exists no dew-insoluble corrosion products.

The SO_2 dry deposition velocity is defined using the following equation:

$$F_{SO_2} = [SO_2]V_d, \tag{2}$$

where F_{SO_2} is the molar flux of SO_2, and V_d is the dry deposition velocity. During the exposure experiments, the flux of SO_2 was not measured. However, if it is assumed that all of the SO_2 deposited during the wet period solubilizes into the dew and the SO_2 deposited during the dry conditioning period (t_d) can be ignored (see discussion below), Equation (2) can be used to calculate V_d by equating F_{SO_2} and $F_{SO_4^{2-}}$. Figure 3 shows a plot of $F_{SO_4^{2-}}$ vs $[SO_2]$. The slope yields a value of 0.90 cm s^{-1} for the dry deposition velocity. The intercept is -1.03 nmol cm^{-2} h^{-1} and the correlation coefficient (R^2) is 0.996.

To determine the amount of deposition taking place during the dry conditioning period, at least one panel was kept dry (no dew formation) during each of the experiments. The surface densities of SO_4^{2-} were obtained by analyzing the (deionized H_2O) spray rinse and are shown in Table 4. The densities are essentially independent of $[SO_2]$ which is consistent with the panels becoming saturated with SO_2. The surface

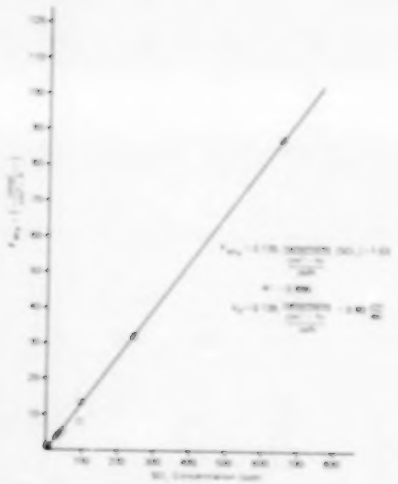

Fig. 3. Dew SO_4^{2-} flux as a function of SO_2 concentration.

Table 4. Summary of saturation fluxes, molecular radii of deposited sulfur species and the times required to saturate a dry panel of galvanized steel

$[SO_2]$ (ppb)	Saturation density $\rho^s_{SO_4^{2-}}$ (nmol cm^{-2})	Molecular radius (r) (Å)	Saturation time (t_s)* (h)
3	1.6	1.8	8.0
7	0.6	2.9	3.4
30	1.2	2.1	0.8
45	0.7	2.8	0.5
650	3.0	1.3	0.04

The radii are calculated using Equation (3) and the saturation time by equation (6).
$\bar{R} \pm \sigma_R = 2.2 \pm 0.7$ Å.
*The average value for $\rho^s_{SO_4^{2-}}$ has been used to calculate t_s.

density calculations assume that all of the deposited SO_2 is washed off during the rinse. The average surface density is 1.4 ± 1.0 nmol cm^{-2}. To determine whether this density is consistent with the presence of a monolayer of adsorbed SO_2, the average radius of the molecules comprising the monolayer was calculated using the following equation:

$$\pi r^2 = (\rho^s_{SO_4^{2-}})^{-1}, \tag{3}$$

where $\rho^s_{SO_4^{2-}}$ is the SO_4^{2-} saturation surface density and r is the molecular radius. The results are shown in Table 4. The average radius of 2.2 ± 0.7 Å agrees with the literature value of 2.2 Å (Judeikis *et al.*, 1978) and, therefore, is consistent with the assumption that the saturation density corresponds to a monolayer of adsorbed SO_2. The time required to reach saturation during the dry period is calculated by assuming that the surface density of SO_2 satisfied the following differential equation:

$$\frac{d\rho_{SO_2}}{dt} = [SO_2]V_d(1-\theta), \tag{4}$$

where ρ_{SO_2} is the surface density of SO_2, and θ is the covering ratio which is equal to $(\rho_{SO_2}/\rho^s_{SO_2})$ where $\rho^s_{SO_2}$ is the SO_2 surface saturation density. The term $[SO_2]V_d$ is the flux of SO_2 to the surface when the deposition velocity is controlled by the gas-phase resistance, i.e. the surface resistance is 0. The term $1-\theta$ is introduced into Equation (4) as a way of adding a surface resistance term such that the uptake of SO_2 decreases as the density approaches the saturation value.

The solution to Equation (4) is

$$\rho_{SO_2}(t) = \rho^s_{SO_2}\left[1 - \exp\left(\frac{-[SO_2]V_d t}{\rho^s_{SO_2}}\right)\right]. \tag{5}$$

The time required for $\rho_{SO_2}(t)$ to reach 90% of $\rho^s_{SO_2}$ is

$$t_s = \frac{2.3\rho^s_{SO_2}}{[SO_2]V_d}. \tag{6}$$

The SO_2 saturation times are shown in Table 4. The

times range from 8 h for the 3-ppb SO_2 experiment to 2 min for the 650-ppb SO_2 experiment.

These results can be employed to determine the amount of SO_2 adsorbed during the dry conditioning period by calculating $\rho_{SO_2}(t_d)$ using Equation (5). The results can be compared with the amount of SO_2 deposited during the entire exposure period. The results, shown in Table 5, demonstrate that the correction due to SO_2 deposited during the dry conditioning period should not significantly affect the calculation of the dry deposition velocity obtained from the slope in Fig. 3.

In Fig. 4, the Zn flux (F_{Zn}) is plotted against $F_{SO_2^-}$. A linear least squares fit to the data gives a value of 1.06 for the slope, −0.64 nmol cm^{-2} h^{-1} for the intercept, and 0.995 for the correlation coefficient. Since it has been assumed that all of the deposited SO_2 appears as SO_3^{2-} or SO_4^{2-} in the dew, the slope gives the effective stoichiometry β for the reaction between SO_2 and Zn on the surface. The result is consistent with the model that each deposited SO_2 molecule reacts with one Zn molecule (Haynie, 1980). However, the result does not define the specific electrochemical reactions that give rise to this value for β.

Wet deposition

A summary of the rain rinse data is displayed in Table 6. The Zn concentration in the rain rinse is shown for pHs of 5.6, 5.0, 4.7, 4.0, 3.7 and 3.0 for the 3-ppb, 30-ppb and 45-ppb SO_2 experiments. Two sets of data are included for the 30-ppb SO_2 experiment. At the end of the experiment one set of panels was sprayed with 50 ml of the experimental concentration and another set with 100 ml. It is convenient to express the Zn flux in nmol cm^{-2} cm$_r^{-1}$, i.e. the number of nanomoles of Zn dissolved into the rain per cm^2 of panel per cm of rain (cm$_r$). This flux is numerically equal to the Zn concentration in nmol ml^{-1}.

Table 5. Comparison between the amount of SO_2 deposited during the dry conditioning period and the amount deposited during the entire exposure period

$[SO_2]$ (ppb)	$\rho(t_d)$ (nmol cm^{-2})	$\rho(t_e)$ (nmol cm^{-2})
3	1.4	8.2
7	1.4	12.6
30	0.3	26.6
45	1.4	31.5
95	1.4	46.9
250	1.4	542.3
0	1.4	646.8

Figure 5 shows the dependence of the Zn flux (F^{R}_{Zn}) on the rain pH for the 30-ppb SO_2 experiment. The Zn flux increases by less than a factor of two as the pH drops from 5.6 to 4.0. Between pH 4.0 and 3.0, the Zn flux increases by nearly an order of magnitude. Plots F^{R}_{Zn} vs F^{R}_{H} for the 3-ppb, 30-ppb and 45-ppb SO_2 experiments are shown in Fig. 6 in which F^{R}_{H} is the incident rain H^+ flux (nmol cm^{-2} cm$_r$). The 50-ml and 100-ml spray data for the 30-ppb SO_2 experiment were averaged. Linear least squares analysis was conducted for each experiment. The following are the equations for the fits:

$$[SO_2] = 3\ \text{ppb} \quad F^{\mathrm{R}}_{Zn} = 0.097\,F^{\mathrm{R}}_{H} + 19.5 \qquad R^2 = 0.978; \quad (7a)$$

$$[SO_2] = 30\ \text{ppb} \quad F^{\mathrm{R}}_{Zn} = 0.059\,F^{\mathrm{R}}_{H} + 4.03 \qquad R^2 = 0.999; \text{ and} \quad (7b)$$

$$[SO_2] = 45\ \text{ppb} \quad F^{\mathrm{R}}_{Zn} = 0.021\,F^{\mathrm{R}}_{H} + 3.85 \qquad R^2 = 0.976. \quad (7c)$$

The differences in the slopes and intercepts show that the corrosion induced by the spray depends on the

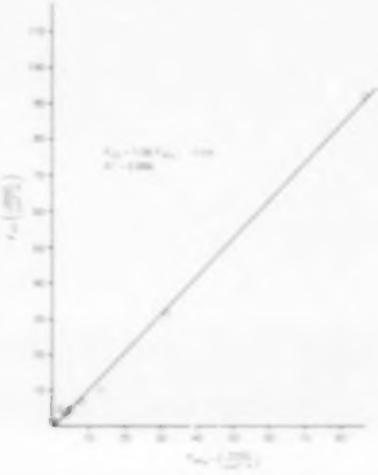

Fig. 4. Dew Zn flux as a function of dew SO_2 flux.

Table 6. Chemical composition of rain rinse

$[SO_2]$ (ppb)	Volume of rain (ml)	[Zn] (nmol ml^{-1})					
		pH* = 5.6	pH = 5.0	pH = 4.7	pH = 4.0	pH = 3.7	pH = 3.0
3	50	17	15	18	34	48	114
30	50	4	3	6	9	14	59
30	100	3	5	6	10	20	67
45	20	6	4	4	4	8	25

*pH of incident rain.

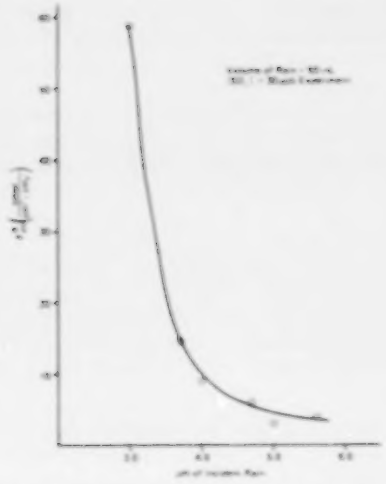

Fig. 5. Rain Zn flux as a function of incident rain pH.

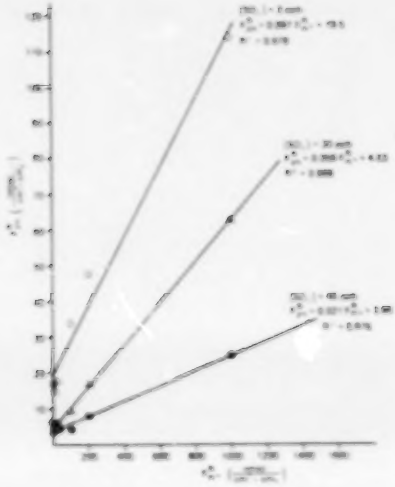

Fig. 6. Rain Zn flux as a function of incident hydrogen ion flux for SO_2 concentrations of 3, 30 and 45 ppb.

exposure history of the panel. In addition to H^+, the acid spray contained NH_4^+ and SO_4^{2-} which have concentrations proportional to $[H^+]$. From these experiments it is not possible to pinpoint the species responsible for the corrosion.

4. DISCUSSION

The experimental results obtained in these short-term exposure experiments indicate the following points:

1. The total flux of SO_2 rather than the ambient concentration should be employed to construct damage functions.
2. When a fresh surface is dry, SO_2 will be adsorbed until an amount similar to a monolayer has deposited. In the presence of a film moisture, no saturation occurs and the deposition is controlled by the gas-phase resistance of the atmosphere.
3. There exists 1:1 relationship between the number of SO_2 molecules deposited onto the surface and the number of Zn molecules that dissolve into the dew.
4. The spraying of exposed samples induces corrosion. The extent of corrosion for a fixed H^+ flux appears to depend on the exposure history of the samples.

The results will be discussed in terms of how they can be used to estimate the relative importance of physical and chemical processes that affect the atmospheric corrosion of galvanized steel and to examine whether previously constructed damage functions are consistent with these estimates.

The total amount of SO_2 deposited during a dry period of duration (t_d) followed by a period of wetness (t_w) is determined by the following equation:

$$\rho_{SO_2} = \rho_{SO_2}^s \left(1 - \exp\left[\frac{-[SO_2]V_d t_d}{\rho_{SO_2}^s}\right]\right) + [SO_2]V_d t_w. \quad (8)$$

Consider a 24-h period, where the galvanized steel samples are dry for the first 19 h and are wet for the remaining 5 h due to the presence of dew. Assume that the surface is exposed to a continuous supply of SO_2 at a concentration of 4 ppb with a deposition velocity of 0.90 cm s^{-1}. The amount of SO_2 deposited during the dry period is 1.4 nmol cm^{-2}, the saturation density. The contribution during the wet period is 2.7 nmol cm^{-2}; therefore, the total SO_2 deposited is 4.1 nmol cm^{-2} (66% is deposited during the wet period and 34% during the dry period). If an SO_2 concentration of 45 ppb, a level typical of a polluted industrial area, is assumed, application of Equation (8) gives 1.4 and 30.3 nmol cm^{-2} for the dry and wet contributions, respectively. These results demonstrate that for relatively high concentrations of SO_2, the deposition occurring during dry periods can be ignored; however, as the SO_2 concentration decreases, the contribution due to the build up of a monolayer can represent a substantial contribution to the total deposition. However, it is difficult to extrapolate these results to actual environmental conditions because the adsorptive capacities of a panel exposed to dew and rain may differ substantially from that of a fresh panel.

The effective stoichiometry of the reaction between adsorbed SO_2 and Zn on a wet surface is one. Therefore, the amount of corrosion caused by SO_2 (dew soluble component) can be calculated if the amount of SO_2 deposited is known and the residence

time of the SO_2 on the surface is long enough so that all the SO_2 reacts. Since time of wetness associated with dew formation is in the order of hours, there is ample time for the SO_2 to react. The laboratory-derived value for the stoichiometric constant β can be compared with that obtained by Haynie (1980) who conducted a statistical analysis of corrosion rates of galvanized steel in the St. Louis area. In the study, dry deposition velocities were calculated from logarithmic wind velocity vs height distributions. Regression analysis yielded a stoichiometric constant of 1.087 ± 0.283, in excellent agreement with the results obtained here.

In addition, Haynie fitted the St. Louis data to a damage function having the form

$$C_{Zn} = (A + B[SO_2])t_w, \tag{9}$$

where C_{Zn} is the Zn corrosion rate in $\mu m\ y^{-1}$; t_w is the time of wetness in years; $[SO_2]$ is the average SO_2 concentration in $\mu g\ m^{-3}$; and A and B are regression coefficients. The functional form is a modified version of the linear bilogarithmic law for atmospheric corrosion. It assumes that the weight loss is related to the exposure time by

$$p = Ct^D, \tag{10}$$

where p is the weight loss per unit area; t is the total exposure time; and C and D are obtained by performing a linear regression analysis on the equation $\log p = D \log t + \log C$ (Pourbaix, 1982). In Equation (10), a value of 1 has been assumed for the exponent D and the time dependence has been expressed in terms of time of wetness rather than exposure time.

Values for A and B obtained by Haynie (1982) are shown in Table 7. Also included are values for the regression coefficients obtained from analysis of field data from the Soviet Union (Mikailvosky, 1982) and Scandanavia (Atteraas and Haagenrud, 1982). The theoretical value for B, assuming a deposition velocity of 1 cm s^{-1} and $\beta = 1$, is $0.045\ \mu m\ a^{-1}\ \mu g^{-1}\ m^{-3}$. Haynie obtained a value of $0.022\ \mu m\ a^{-1}\ \mu g^{-1}\ m^{-3}$ for B. As demonstrated by the agreement between his experimentally found value for β and the 'theoretical' value, i.e. 1, the discrepancy is due to an incorrect choice for the deposition velocity. The result suggests that SO_2 regression coefficients obtained from different data sets cannot be compared unless differences in deposition velocities are taken into account.

Table 7. Field data regression coefficients for Equation (10)

Field study	A ($\mu m\ y^{-1}$)	B ($\mu m\ y^{-1}\ \mu g^{-1}\ m^{3}$)
St. Louis*	2.36	0.022
Scandanavia†,‡	1.58	0.078
Soviet Union§,‖	3.92	0.067

*Haynie (1980)
†Atteraas and Haagenrud (1982)
‡It has been assumed that the fractional time of wetness is 0.4
§Mikailvosky (1982)
‖In the formalism developed by Mikailvosky, the coefficient A depends on the temperature. A value of 15°C was chosen.

The values for B of $0.067\ \mu m\ a^{-1}\ \mu g^{-1}\ m^{-3}$ found by Mikailvosky (1982) and $0.078\ \mu m\ a^{-1}\ \mu g\ m^{-3}$ obtained by Atteraas and Haagenrud (1982) are consistent with the 'theoretical' value if the deposition velocity is 1.5 cm s^{-1}.

The remaining term in Equation (9) accounts for the corrosion that is not associated with SO_2. Table 7 gives numbers ranging from 1.58 to $3.92\ \mu m\ a^{-1}$ for the coefficient A. The parameter A/B gives the concentration of SO_2 that is required to contribute the same amount of corrosion as that associated with all processes other than SO_2 deposition. The equivalent SO_2 concentrations found were 22 ppb (Soviet Union), 8 ppb (Scandanavia), and 40 ppb (St. Louis). The intercept term represents a substantial contribution to the overall corrosion rate, especially in areas where the ambient $[SO_2]$ is low. In the United States, the average urban $[SO_2]$ is ~8 ppb (U.S. Environmental Protection Agency, 1983). However caution must be used in interpreting A. If the data set contains a few high $[SO_2]$/Zn corrosion data points, the regression analysis will be dominated by these data points and the intercept generated will be of limited value. If damage functions are to be used to predict corrosion rates, they should be generated with a data set that contains similar $[SO_2]$.

Field experiments have shown that chlorides accelerate the atmospheric corrosion of galvanized steel (Atteraas and Haagenrud, 1982). This contribution, which is highly significant in marine areas, should be represented in the damage function as a separate term and not included in A. This methodology was employed by both Mikailvosky (1982) and Atteraas and Haagenrud (1982). Chlorides should play a minimal role in corrosion in St. Louis because of its inland location. The impact of particulate sulfate has not been examined in detail but, because particulate sulfate dry deposition velocities are small compared with those associated with SO_2, the contribution of particulate sulfate is likely to be small relative to SO_2 (Harker *et al.*, 1980). The role of other atmospheric contaminants such as HNO_3 is not known, and further research is required.

Two elements that may contribute to A are the corrosion associated with clean air and wet deposition. In the presence of a moisture film, but in the absence of air pollutants other than CO_2, the effective operative electrochemical reactions taking place on the surface are believed to be (Nriagu, 1978):

Anode

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Cathode

$$2H^+ + 2e^- \rightarrow H_2.$$

The zinc hydroxide ($Zn(OH)_2$) formed will react with dissolved CO_2 to produce water-insoluble zinc carbonate ($ZnCO_3$). Build up of the insoluble corrosion products such as $Zn(OH)_2$ and $ZnCO_3$ will create a protective layer that serves to inhibit further corrosion. The rate of corrosion will then be small unless there is some means for either preventing the formation of the protective layer or destroying it once it has formed. One mechanism for removing the protective layer is the reaction of active species in acidic rain (i.e. rain with a pH low enough to dissolve the layer) with the layer compounds. However, the protective layer will form again during the next clean air dew period after the rain event. Each dew/acid rain cycle will produce additional corrosion. An estimate of the size of the effect can be made by using the linear least squares fit for the 3-ppb SO_2 exposure/spray experiment [Equation (7a)]. For a pH = 4, $F_{H^+} = 100$ nmol cm^{-2} cm$_r^{-1}$ and $F^R_{Zn} = 29$ nmol cm^{-2} cm$_r^{-1}$. If the yearly rainfall is 100 cm, the calculated value for the Zn corrosion due to rain is 2900 nmol cm^{-2} which is equivalent to 0.3 μm a^{-1}. The application of Equation (7a) to estimate the rain contribution assumes that the corrosion product composition of exposed galvanized steel is similar to that of the 3-ppb SO_2 exposure/spray experiment, since the exposures conducted at 30 ppb and 45 ppb SO_2 showed that the corrosion efficiency depends on the exposure history and, in addition, the surface residence times of the rain are similar to the ones employed in the laboratory. The results suggest that acid deposition contributes to corrosion and can account for at least some of the corrosion not associated with dry deposition of SO_2. They are consistent with field results that show Zn corrosion in the absence of measurable amounts of SO_2 (Haynie, 1980).

In the presence of relatively large concentrations of SO_2, the major corrosion product will be soluble $ZnSO_4$ and no protective layer will form. Additional corrosion is induced during a rain event. The dependence of the corrosion efficiency on the exposure history suggests that the wet deposition corrosion mechanism in the absence of a protective layer differs from that occurring in a clean air environment and may involve reactions of the active species in the rain with the base metal.

The experimental results do not address the question as to whether the major electrochemical/chemical reactions that control the corrosion rate are the same for the corrosion induced by dry and wet deposition. However, the results can be used to compare the effective stoichiometries for the reaction of Zn and H^+ for dew and rain if it is assumed that each dissolved SO_2 molecule produces two H^+. The effective dew stoichiometry in terms of H^+ is 0.53. The effective rain stoichiometries are found by dividing Equations (7a)–(7c) by $F^R_{H^+}$ and, in contrast with the dew stoichiometry, depend on incident H^+ flux or equivalently the pH of the rain. For a pH = 4.7, the effective rain stoichiometries (the number of moles of Zn corroded per mole of H^+ deposited) for the 3-, 30- and 45-ppb SO_2 experiments are 1.1, 0.3 and 0.2, respectively, whereas for pH = 4.0, the stoichiometries are 0.3, 0.1 and 0.1, respectively.

5. CONCLUSIONS

The results show that short-term laboratory exposure experiments can be used to gain insight into the aerodynamic and chemical processes that control the atmospheric corrosion of galvanized steel. Much of the information has been gained from analyses of dew and rain rinses. It appears that the corrosion due to dry deposition of SO_2 can be calculated by equating the SO_2 flux to the Zn flux. It has also been demonstrated that SO_2 will deposit onto a fresh dry panel until an amount similar to a monolayer has been adsorbed.

Analysis of the rain rinse shows that acidic deposition contributes to the corrosion. The contribution appears to depend on the exposure history of the sample. It was also shown that wet deposition of acidic species can contribute to the damage via a model where the protective layer is cyclically removed due to reaction with chemical species contained in the acidic rain.

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